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Appendix C

Title: Using Elastomeric Membranes as
Dry Resists and for Dry Lift-Off

Using Elastomeric Membranes as Dry Resists and for Dry Lift-Off

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Elastomeric membranes that contained regular arrays of well-defined holes were formed by spin-coating a prepolymer onto a photolithographically defined master. These membranes were used as dry resists or as masks in dry lift-off to produce simple features as small as 5 μm on both planar and nonplanar surfaces. These procedures were “dry” because the membranes conformed and sealed reversibly to surfaces: no solvent was required either to deposit the membrane or to remove it from the substrate. A variety of materials, some of which would be difficult to pattern using conventional methods, were patterned using this technique. These materials included metals, sol-gels, hydrogels, biological macromolecules, and organometallic molecules. The membranes were used in sequential, dry-lift off steps to produce structures with greater complexity than those generated with a single membrane.

Introduction

This paper describes the use of elastomeric membranes to pattern a range of materials at the 5- μm scale. The membranes are used as a dry resist layer and in a dry lift-off procedure. These methods offer alternatives to standard pattern transfer techniques for fabrication based on photolithography and lift-off. We believe that these approaches to microfabrication will be especially useful in patterning materials that are incompatible with conventional processing steps and for patterning nonplanar surfaces.

Most methods for microfabrication begin by using photolithography to form a pattern in photoresist on a substrate. This patterned photoresist performs one of two functions in subsequent steps: it either acts as a resist (for example, against wet-chemical etching, reactive ion etching (RIE), ion implantation, or electrodeposition), or it serves as a mask for a lift-off step. Lift-off refers to a procedure in which a material (usually a metal) is deposited from the vapor phase onto the entire surface of a substrate patterned with photoresist, and the photoresist is then dissolved to leave the material in patterned form: as the photoresist dissolves, it “lifts-off” the layer that has been deposited on it.¹ Although these techniques are very widely used, some important classes of materials—biological materials, gels, some polymers, low molecular weight organic and organometallic species—are often incompatible with them: to pattern these materials successfully, the patterned photoresist must be impermeable to the reagents used in deposition, the deposited material must not be affected by the solvents used to remove the photoresist, and the substrate (and any structures already on it) must not be altered by the processing steps.

Alternatives to photolithography often involve a shadow mask,^{1–3} typically formed from a rigid metal,⁴ in the pattern transfer step. In these systems, an air gap always

exists between the mask and substrate:¹ this gap can give rise to features larger than the holes in the mask because of lateral diffusion and oblique deposition during evaporation and makes the use of rigid shadow masks to pattern materials from solution impossible.

Here, we describe a method for micropatterning that uses an elastomeric mask fabricated from poly(dimethylsiloxane) (PDMS) in place of a patterned layer of photoresist. This elastomeric membrane is fabricated by spin-coating a liquid PDMS prepolymer onto a “master” consisting of features of photoresist on a silicon wafer. Because the membrane can conform to and seal reversibly against the contours of a surface with which it is in contact, and because it is chemically unreactive, it can function both as a dry resist and as a mask for dry lift-off. Both procedures are “dry” because no solvents are required either to deposit the patterned mask onto the surface or to remove it from the surface.

At its present state of development, this approach has strengths and weaknesses. Its strengths are that it solves issues of compatibility associated with conventional patterning and makes it possible to pattern classes of materials that cannot be patterned easily by photolithography or using shadow masks. Its current limitations are that it cannot make small (<1 μm) features and with a single elastomeric membrane, there are constraints on the features that can be produced because the membrane must be continuous, self-supporting, and mechanically stable.

Features in the membrane must be relatively simple, solid, and discrete. This limitation can be addressed by the use of two or three membranes in sequential, registered, dry lift-off steps that allow the fabrication of complex patterns. We believe this method offers a useful new capability in the fabrication of displays,^{5–9} sensors,

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(4) We have shown previously (Xia, Y.; Kim, E.; Whitesides, G. M. *Chem. Mater.* **1996**, *8*, 1558–67; Xia, Y.; Tien, J.; Qin, D.; Whitesides, G. M. *Langmuir* **1996**, *12*, 4033–8) that rigid, polymeric meshes can also be formed by micromolding polyurethane.

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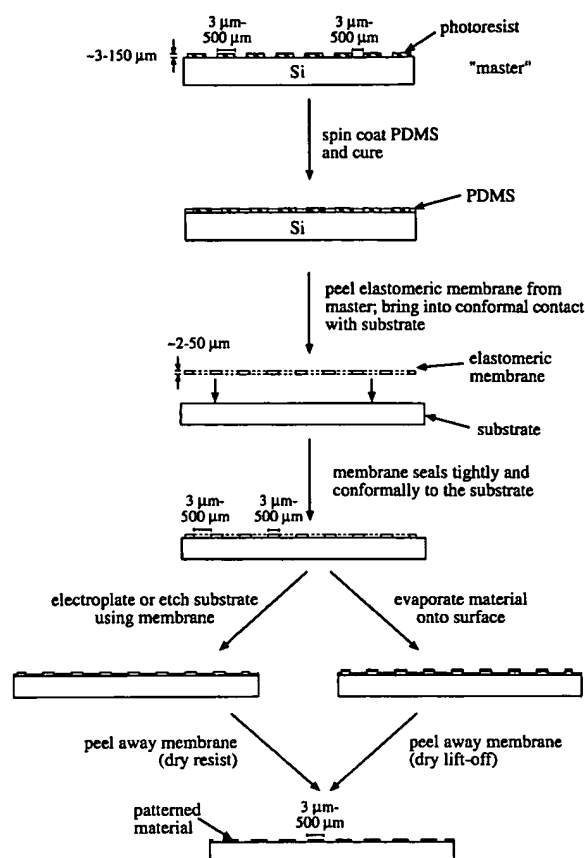


Figure 1. Schematic illustration of the fabrication of elastomeric membranes and their use as dry resists and in a dry lift-off procedure. Spin-coating a liquid prepolymer of PDMS at an appropriate speed onto a master, consisting of posts of photoresist patterned on a silicon wafer by photolithography, resulted in a layer of polymer that was thinner than the posts of photoresist. After curing the elastomer at 65 °C for 1 h, we removed the flexible membrane from the master by peeling: the membrane contained an array of holes that replicated the posts around which they were molded. We have formed membranes with holes ranging from 3 to 500 μm , spaced from 3 to 500 μm , respectively. When an elastomeric membrane was brought into contact with a substrate, a tight, reversible, and conformal seal formed between the two surfaces. The membrane was then used as a resist against etching, electrodeposition, or other processes (left). Alternatively, materials can be deposited onto both the exposed regions of the substrate and the membrane (right), and a dry lift-off step (i.e., peeling the membrane away from the surface) then left material patterned on the substrate.

arrays of microreactors¹⁰ or microelectrochemical reactors, and systems for performing biological assays.

Results and Discussion

Fabrication and Application of Membranes. Figure 1 illustrates schematically the fabrication of the elastomeric membranes and their use both as dry resists and for dry lift-off. We have used a related method previously

for the fabrication of stamps and molds for soft lithographic techniques.¹¹ Here, an array of discrete patterns ($\sim 5\text{--}50\ \mu\text{m}$ thick) formed in photoresist on a silicon wafer functioned as a master. To produce membranes, we spin-coated a prepolymer of PDMS (an elastomer) onto the master at a speed that resulted in the formation of a layer of PDMS that was thinner than the features of photoresist on the master. After curing the prepolymer, we peeled the elastomeric membrane from the master. For the thinner membranes ($<50\ \mu\text{m}$ thick), in a second step, a border of prepolymer "painted" and cured around the pattern of interest facilitated removal of the membrane from the master and made its handling easier. For thicker membranes, the membrane was stable enough that a reinforcing support was generally unnecessary.

Figure 2A shows an optical micrograph of one of these membranes held in a pair of tweezers. When brought into contact with many substrates,¹² these membranes wet the surface and form a tight, reversible seal against it. Figure 2B shows a scanning electron micrograph (SEM) of a section through a similar membrane (50 μm holes, spaced by 50 μm) sealed against a silicon substrate. The smallest features we have produced to date using this technique are 5 μm diameter circles separated by 10 μm (Figure 2C). As is visible in Figure 2B, the top side of the membrane is not flat—there is a meniscus around each feature. During spin-coating, the prepolymer tended to wet the sides of the features of photoresist, so the thickness of the membrane between a set of four posts was less than that adjacent to a post. For thinner membranes (Figure 2C), this effect is less pronounced.

The strength of the seal that forms between these elastomeric membranes and substrates that they contact is key to their use as dry resists and for dry lift-off: this seal is sufficiently strong that it prevents either deposition of materials onto the surface or removal of material from the surface but is sufficiently weak that it can be reversed by peeling the membrane away using a pair of tweezers, after material has been deposited, without damage to the substrate. The thicker elastomeric masks were typically reusable, as are the masters from which they were prepared. The membranes tended to fail by tearing; generally, we were able to reuse the thicker membranes more than five times before visible wear or degradation in performance was observed. The thinner ($<10\ \mu\text{m}$) membranes tended to tear during the removal step and so were only used once. The low cost and ease ($<2\ \text{h}$) of making these membranes, however, means that using a membrane only once is not problematic.

Several factors determined the thicknesses of the elastomeric membranes formed by this technique: speed and duration of spin-coating; lateral dimensions and spacing of features on the master; and the viscosity of the PDMS prepolymer (which changes as a function of time¹³). Figure 2D illustrates that for a given master (50 μm diameter circles, spaced by 50 μm), a given spin speed (3000 rpm) and PDMS mixed and degassed in vacuo for approximately 20 min before spin-coating, the membrane thickness varied between 26 and 53 μm (at a minimum, i.e., between a set of four holes; and between 45 and 55 μm in the regions immediately adjacent to each feature) for different periods of spin-coating. When spin-coating for periods less than 50 s, the thickness of the membrane

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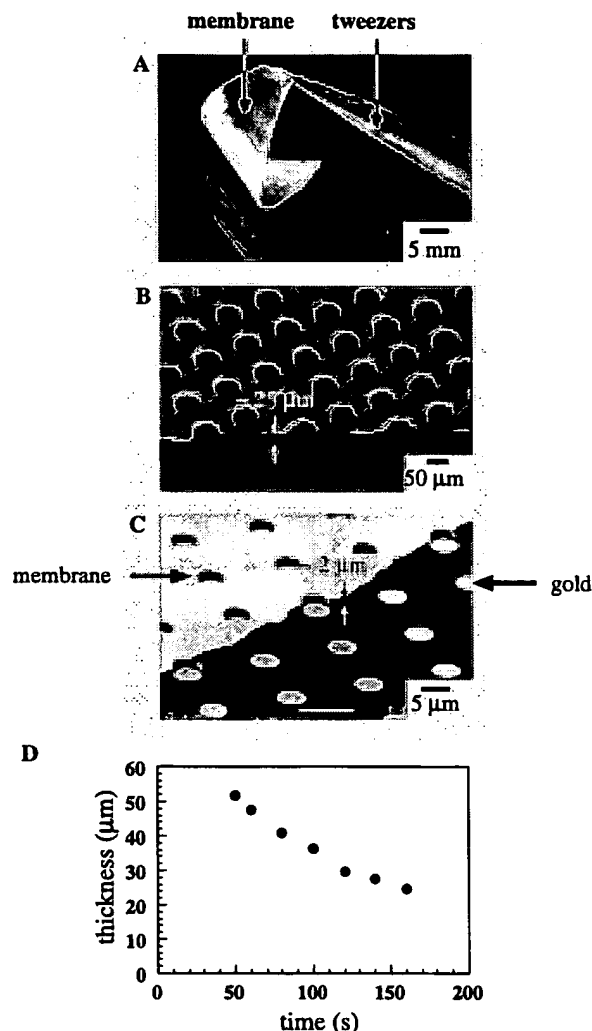


Figure 2. Elastomeric membranes formed by spin-coating on photolithographically defined masters. (A) Optical micrograph of an elastomeric membrane containing 50- μm holes, spaced by 50 μm on a square lattice ($\sim 50 \mu\text{m}$ thick). Membranes were manipulated using tweezers. (B) Scanning electron micrograph (SEM) image of a section through an elastomeric membrane (50- μm holes, spaced by 50 μm) on a silicon substrate. (C) SEM image of a section through an elastomeric membrane (5- μm holes, spaced by 10 μm ; $\sim 2 \mu\text{m}$ thick) sealed conformally against a silicon substrate. We had deposited titanium (Ti, 5 nm) and then gold (50 nm) through the membrane. The image shows an adjacent section where the membrane has been removed. The image shows both the features in the membrane and the features they produce. (D) Spinning speed, spinning time, and the geometrical dimensions and position of features of on the master determined the thickness of the PDMS membrane. For a master with 50- μm diameter circles spaced by 50 μm on a square lattice ($\sim 55 \mu\text{m}$ thick photoresist), we plotted the thickness of the membrane as a function of duration of spin-coating (at a constant speed of 3000 rpm). For durations between 50 and 160 s, the membranes were self-supporting and contained circular holes.

was greater than the height of the features of photoresist on the master: the film of PDMS contained no holes. Spin-coating for more than 160 s resulted in defects in the membranes that were significantly larger than the features. For times between 50 and 160 s, the membranes were self-supporting and contained open holes; we typically used membranes at the thicker end of this range to facilitate handling.

Placing a drop of 2-propanol or ethanol onto a membrane after bringing it into contact with a substrate also aided in handling, because it minimized van der Waals

attractions between surfaces of the membrane and hence the tendency of the membrane to stick to itself.¹⁴ A second method that lessened the problem of self-adhesion was the addition of a second layer of a nonelastomeric polymer to the elastomeric membrane: typically, we spin-coated a layer of epoxy onto the PDMS before its removal from the master, and controlled the combined thickness of the two layers to be less than that of the posts on the master. This composite membrane did not tend to stick to itself, was less likely to be distorted than a PDMS membrane, but still maintained its ability to seal against both planar and nonplanar substrates.

Modification of Interfacial Properties of Membranes To Facilitate Wet-Chemical Patterning.

When a membrane is brought into contact with a substrate, microwells form that have walls defined by the channels in the membrane and bottoms defined by the substrate (Figure 1). When patterning materials from the liquid phase by using elastomeric membranes, in order that reagents can react with or adhere to the substrate, it is critical that the solution of interest fills these microwells. Untreated PDMS has a low surface free energy ($\gamma_{\text{sv}} \sim 21 \text{ dyn/cm}$),¹⁵ so most polar liquids will tend to bead up on a PDMS substrate. We have, however, shown previously¹⁰ that this property can be used to fill microwells formed in PDMS by a technique we called discontinuous dewetting. In discontinuous dewetting, a solution is allowed to drain off an array of microwells either by gravity or by pulling the array from a bulk solution. For most solutions, the liquid will dewet from the surface of the PDMS; when it reaches a geometrical discontinuity in the surface of the substrate (i.e., the edge of a microwell), the liquid becomes pinned, and as the liquid continues to drain, a drop of liquid remains trapped in the microwell. If the array is filled by pulling it from solution, the wells remain filled with approximately equal volumes of solution.¹⁰ When water or aqueous solutions are used, the free energy of the solution is often so high that air bubbles become trapped in the wells. Oxidizing the surface of the PDMS with a plasma treatment increases its surface free energy ($\gamma_{\text{sv}} \sim 59 \text{ dyn/cm}$),¹⁵ makes it more easily wet by solutions, and lessens the likelihood of bubbles being trapped in the wells. In addition, air bubbles can be removed by placing a drop of the solution of interest over the membrane/substrate and placing the system briefly (10–20 s) under vacuum.

Elastomeric Membranes as Dry Resists. When these membranes are in contact with a surface, they can act as resists against etching and to prevent deposition. Using an elastomeric membrane as a dry resist, we patterned substrates with structures that would have been damaged by the deposition or removal of a layer of photoresist, and we used solutions to pattern the surface that would have dissolved a pattern of photoresist or that would have wicked under a shadow mask. This procedure simplifies the mask deposition step because it simply involves laying the membrane down on the substrate (provided, of course, that registration with another pattern on the surface is not required).

(a) Removal of Substrate by Dry Etching. To form an array of microwells (3 μm diameter, 1 μm deep; $\sim 10 \text{ fL}$ volume) in silicon, we placed an elastomeric membrane containing circular holes on the substrate, performed reactive ion etching (RIE) using an SF_6/O_2 mixture, and

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then peeled the membrane away (Figure 3A). Using a patterned layer of photoresist as the resist against etching would have required performing photolithography directly on the substrate that could bear existing structures sensitive to the conditions used for photolithography. Furthermore, a photoresist mask could only be used for a single sample—it would be dissolved during the removal step. With the dry resist, the patterned layer is placed on the substrate without damage to the underlying layers and, in the case of thicker membranes, it can be reused several times. The use of a rigid shadow mask would have reduced etching of the unexposed regions but would not eliminate it completely because of the air gap between the mask and substrate.

(b) Metals by Electrodeposition. Deposition of metals (and conducting polymers) by electrochemistry is impossible using a nonsealing mask: plating solution wicks between the mask and substrate by capillarity and results in electrodeposition over the entire surface. The use of patterns in photoresist for controlling electrodeposition is practical provided that the resist is compatible with the plating solution; in some cases, it is not. The reversible seal that forms between an elastomeric membrane and a substrate permitted wet-processing steps without liquid wicking between them by capillarity; these membranes are less susceptible to dissolution than photoresist.¹⁶ Electroplating through membranes supported on a conductive substrate formed metallic structures (Figure 3B). Metal deposited only onto the unmasked regions of the substrate during electrodeposition.

(c) Organically Modified Silicates (ORMOSILS) by Sol-Gel Methods. Structures formed from glassy materials are useful in the fabrication of Fresnel lenses or gratings,¹⁷ waveguides,¹⁸ and microlasers.¹⁹ The conditions required for the fabrication of ceramic structures by sol-gel processing (Figure 3C) make them difficult to fabricate by other methods. Here, to produce structures in an organically modified silicate,²⁰ we covered a surface (defined by the substrate and the membrane) with a solution of 3-glycidopropyltrimethoxysilane/oxalic acid that contained a drop of ammonium hydroxide. This solution dewetted from a flat PDMS substrate. Since the surface contained wells, when the solution dewetted it, solution remained trapped in the wells. Using most conventional photoresists to pattern this material would be impossible because the basic (pH ~11) conditions required for condensation of the gel would degrade the photoresist layer. A rigid shadow mask could also not be used for patterning because the solutions would wick between the membrane and substrate by capillarity and coat the entire substrate.

(d) Hydrogels by Dewetting. Patterning an aqueous gel from solution using a rigid shadow mask is difficult for the same reasons as for the other wet chemical techniques: the solution would wick between the mask and substrate. While a hydrogel would be compatible with a patterned organic photoresist, it would be destroyed by the solvents used in lift-off. Elastomeric membranes do, however, function well as masks for patterning these sensitive materials. We sealed a PDMS membrane against

a glass surface that had been cleaned by treatment with an oxygen plasma and placed a drop of an aqueous solution of gelatin at 60 °C on top of the membrane/glass. After the system was evacuated briefly to remove air trapped in the wells and the substrate was brought back to 60 °C, discontinuous dewetting by gravity left solution in the wells. On cooling to room temperature the solution set into a gel, and subsequent removal of the membrane left an array of patterned gelatin on the substrate (Figure 3D). We have also patterned polyacrylamide gels using a similar technique. These patterned gels have potential applications, for example, as components in diffraction-based biological sensors^{21,22} or to create regular arrays of discrete, small features of photographic materials.

Elastomeric Membranes for Dry Lift-Off. "Dry lift-off" is a procedure that involves placing a membrane on the substrate, depositing material over the entire exposed surface, and peeling away the membrane to leave the material patterned on the substrate (Figure 1). Figure 3E–H shows SEMs and optical micrographs of several classes of materials patterned by dry lift-off. The reversibility of the seal between the membrane and the substrate allows the mask to be peeled away from the surface and enables the patterning of materials that would be damaged by exposure to the solvents required for photolithography and conventional lift-off.

(a) Metals by Evaporation. We used a membrane to produce features of gold by dry lift-off (Figures 2C and 3E). Figure 2C shows one section of a substrate still in contact with the membrane and an adjacent section where the membrane has been removed. The image shows both the features in the membrane and the structures they produce.

(b) Organometallic Compounds by Evaporation. Small organometallic molecules, such as tris(8-hydroxyquinoline)aluminum (Alq₃), can be evaporated through shadow masks, or patterned photoresist, but are usually soluble in the solvents used for lift-off.⁵ Several ingenious but complicated methods have been developed for patterning these materials, since they may be useful in optical displays.^{5,7,23} Thermal evaporation of Alq₃ (500 Å), through an elastomeric membrane, followed by dry lift-off, produced circular areas of the material. These patterns are photoluminescent (Figure 3F) and electroluminescent when addressed electrically. We have reported recently that we used this technique to fabricate pixelated optical displays using these electroluminescent materials.²⁴

(c) Biological Materials by Nonspecific Adsorption. Forming patterns of biological materials (for sensing applications or for biological assays, for example) using conventional patterning techniques can be difficult because: (i) when a conventional shadow mask is used, patterning the adsorption of protein from solution is impossible, because the mask does not conformally seal against the substrate; (ii) the solvents required for conventional lift-off denature or desorb biological macromolecules. We and other groups have, however, developed soft-lithographic methods for patterning proteins.^{25–30} Figure 3F

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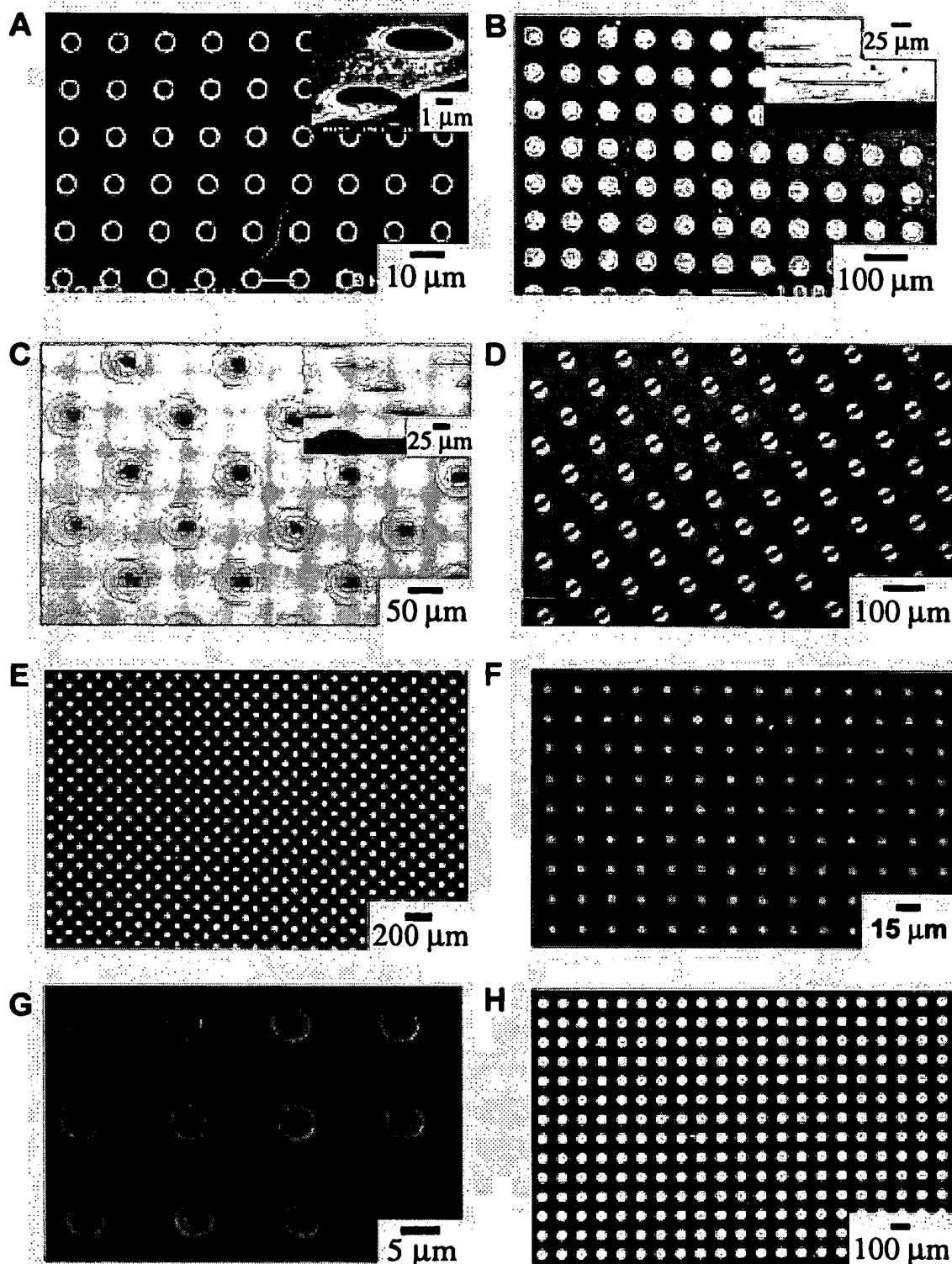


Figure 3. Elastomeric membranes can act as dry resists or for dry lift-off, as shown schematically in Figure 1, to pattern many classes of materials. Details of these experiments are given both in the text and in the Experimental Section. (A) Microwells in silicon ($3\text{ }\mu\text{m}$ diameter, $1\text{ }\mu\text{m}$ deep) formed by reactive ion etching (RIE) using an elastomeric membrane as a resist. (B) SEM image of circular posts ($50\text{-}\mu\text{m}$ diameter) of silver formed on a gold-coated silicon substrate by electroplating silver while using an elastomeric membrane as a resist against electrodeposition. (C) SEM image of circles ($50\text{-}\mu\text{m}$ diameter) of an organically modified silicate (ORMOSIL) formed from a sol-gel precursor using a membrane as a dry resist. (D) Optical micrograph of circles of gelatin formed by using an elastomeric membrane as a dry resist. (E) SEM image of circles of gold ($50\text{-}\mu\text{m}$ diameter) formed by electron-beam evaporation through an elastomeric membrane (the evaporation was two stage—an adhesion promoter (Ti; 5 nm), followed by gold (50 nm) onto a silicon wafer), and a subsequent dry lift-off step. (F) Image of photoluminescence from circles formed by thermal evaporation of tris(8-hydroxyquinoline)aluminum (AlQ_3 ; 50 nm) onto a membrane on a silicon wafer followed by dry lift-off. (G) Fluorescence micrograph of circles ($5\text{-}\mu\text{m}$ diameter) of FITC-labeled bovine carbonic anhydrase, adsorbed onto a gold-coated silicon wafer coated with a self-assembled monolayer of hexadecanethiolate. Protein adsorbed to the substrate and the membrane (which was in conformal contact with the substrate); the dry lift-off step left only the exposed regions of the substrate patterned with protein. (H) Fluorescence micrograph of circles of poly(phenylenevinylidene) (PPV) formed by chemical vapor deposition of a chlorinated xylene (PPV precursor) formed from a monomer (α,α' -dichloro-*p*-xylene) through an elastomeric membrane followed by dry lift-off.

shows a micrograph of circles ($5\ \mu\text{m}$ diameter) of fluorescein isothiocyanate (FITC)-labeled bovine carbonic anhydrase, adsorbed onto a gold-coated silicon wafer coated with a self-assembled monolayer (SAM) of hexadecanethiolate. The PDMS membrane was placed in contact with the SAM, and a drop of a solution of protein was placed on the substrate for 2 h. The protein adsorbed onto both the substrate and the membrane. We drained the excess solution of protein from the substrate, washed and dried the substrate in a stream of nitrogen, and removed the membrane. After dry lift-off, only the exposed regions of the substrate remained patterned. These membranes could also offer a simple method for patterning cells on a surface.

(d) Conducting Polymer Precursors by Chemical Vapor Deposition. When depositing materials by chemical vapor deposition (CVD), no equivalent to conventional lift-off exists and rigid shadow masks are not effective because the shadow mask is not in intimate contact with the substrate: we have found that material will deposit between the mask and the substrate.³¹ Using an elastomeric membrane for dry lift-off, we have patterned a material that can be converted thermally to the conducting polymer, poly(phenylenevinylene) (PPV). In a CVD chamber, we formed a chlorinated xylene (a PPV precursor) on pyrolysis of α,α' -dichloro-*p*-xylene. This precursor condensed on the substrate (which bore a membrane) and partially polymerized. We held the sample at $150\ ^\circ\text{C}$ for about 1 h—this step served to convert further the precursor so that it became more rigid and had improved adhesion to the substrate. After the membrane had been lifted off, the material was fully converted to PPV (Figure 3H). We are pursuing this methodology to create electroluminescent patterns of small features of PPV that could potentially be used in flat-panel displays.³¹

Resolution of Structures Formed by Dry Lift-Off. We have produced large ($>6\ \text{cm}^2$) arrays of circles of gold ($50\text{-}\mu\text{m}$ diameter; 50-nm thickness, supported on a silicon wafer with a 5-nm layer of titanium (adhesion promoter)) by using an elastomeric membrane and dry lift-off (Figure 4A). High-resolution SEM images of a section of these gold circles (images B and C of Figure 4) show that the edge roughness is less than $50\ \text{nm}$: we believe that this number is limited largely by the grain size of the gold and is comparable to that observed using photoresist and conventional lift-off. Figure 4C shows a relatively well-defined feature $\sim 2\ \mu\text{m}$ beyond the outer edge of the circle that we believe is a nanometer-thick layer of lower molecular weight PDMS that distills from the elastomer on heating during the evaporation. We have not observed these deposits when patterning by other techniques and we have not found that this thin layer of material has an effect on the performance of structures made by this technique.

Practical Constraints Limit the Features That a Single Membrane Can Produce. When a single elastomeric membrane is used for patterning, practical constraints on the membrane place limitations on the features that can be produced. The membrane must be continuous, self-supporting, and mechanically stable. These requirements mean that features in a membrane

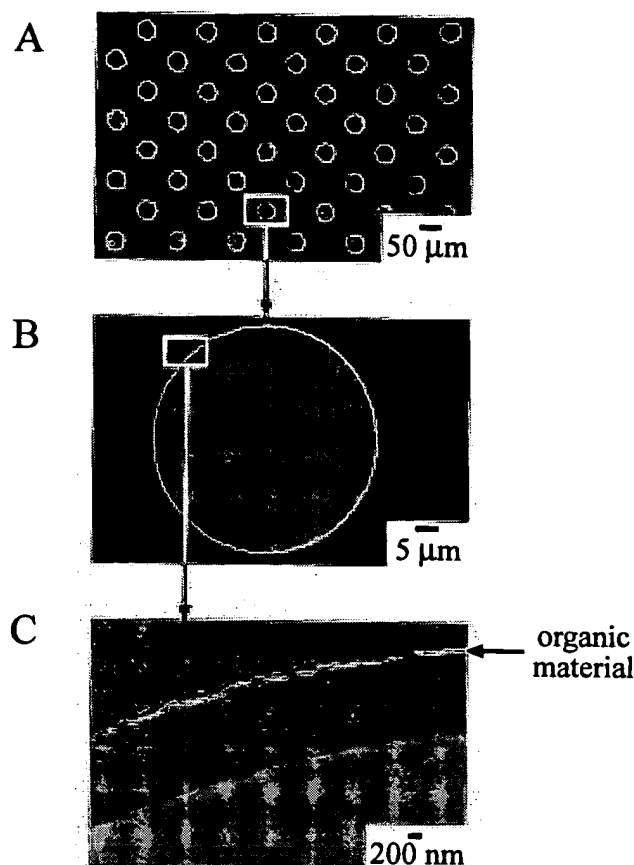


Figure 4. Resolution of structures formed by dry lift-off using an elastomeric membrane. (A) SEM image of circles of gold ($50\text{-}\mu\text{m}$ diameter) formed by electron-beam evaporation through an elastomeric membrane of an adhesion promoter (Ti; $5\ \text{nm}$), followed by gold ($50\ \text{nm}$) onto a silicon wafer and a subsequent dry lift-off step. (B) SEM image of part of a circle of gold shown in Figure 4A. (C) SEM image of a section of a circle of gold shown in Figure 4B.

cannot (i) meet or intersect at their corners, (ii) have a large length-to-width ratio, particularly if features are at a high density (because the supporting membrane between will distort), or (iii) distort out of the plane of the membrane or have a section of membrane that would need to be disconnected from the bulk. Given these restrictions, relatively simple, solid, discrete features are possible, e.g., a solid circle, square, hexagon, or rectangle, provided the length-to-width ratio is small in the case of the rectangle. Figure 5A shows photoluminescence from an alphanumeric pattern that is composed of almost rectangular slots formed by thermal evaporation of tris(8-hydroxyquinoline)aluminum (Alq_3 ; $50\ \text{nm}$) followed by dry lift-off. When two rectangular features intersect, they produce either an L-shaped or cross-shaped opening. Provided the length-to-width ratio is small and the features are small ($<1\ \text{mm}$), the membrane is stable and self-supporting. Figure 5B shows an array of staggered crosses formed using an elastomeric membrane and dry lift-off. The U-shaped opening formed, e.g., by the intersection of three rectangular features, however, is not self-supporting: the "flap" of elastomer will tend to sag laterally. Further, a feature that divides the 2D plane into two pieces, e.g., an open square, which could be formed by the intersection of four slots, or a circular ring of material, is *not* possible to produce with a single mask. Its fabrication would require a membrane that had a disconnected section of elastomer in the center of the feature: this type of membrane is not self-supporting.

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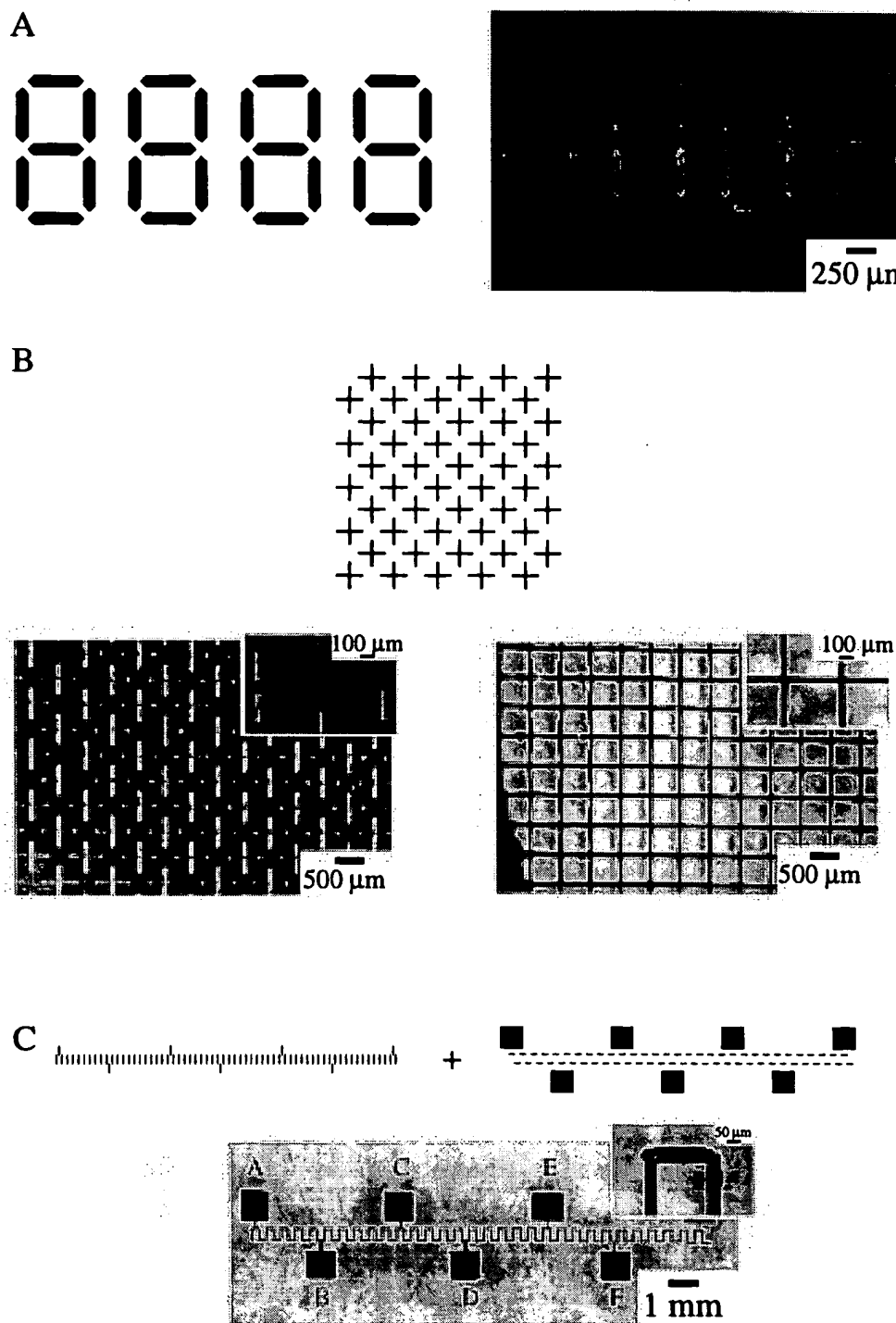


Figure 5. Elastomeric membranes can produce structures with greater complexities than circles. (A) Fluorescence micrograph showing photoluminescence from an alphanumeric pattern formed by thermal evaporation of tris(8-hydroxyquinoline)aluminum (AlQ₃; 50 nm) followed by dry lift-off. (B) Design for an elastomeric membrane that consisted of a staggered array of crosses that produced, after two lift-off steps (with a translation between), a square grid and an optical micrograph of a gold (~50 nm thick) grid. (C) Design for two elastomeric membranes used to produce a serpentine structure in two lift-off steps and an optical micrograph of a gold (50 nm) serpentine structure with contact pads formed on glass.

Multiple Membranes Can Produce Complex Structures. The use of two or three membranes, in a sequence of registered pattern transfer steps, solves the practical limitations on the types of features that single membranes can produce. Parts B and C of Figure 5 illustrate how two membranes, used in sequential dry lift-off steps, can produce more complicated structures. Using a single membrane twice, we evaporated an adhesion promoter (Ti, 5 nm), followed by gold (50 nm) through a membrane

containing an array of staggered crosses, performed dry lift-off once, and then translated the membrane, deposited material again, and performed a second lift-off step to produce a square grid (Figure 5B). In a single step, this pattern would have been impossible to produce because it would have required a mask consisting of a series of disconnected squares. Similarly, two different membranes used in succession produced a gold serpentine structure with contact pads by dry lift-off (Figure 5C). If a single

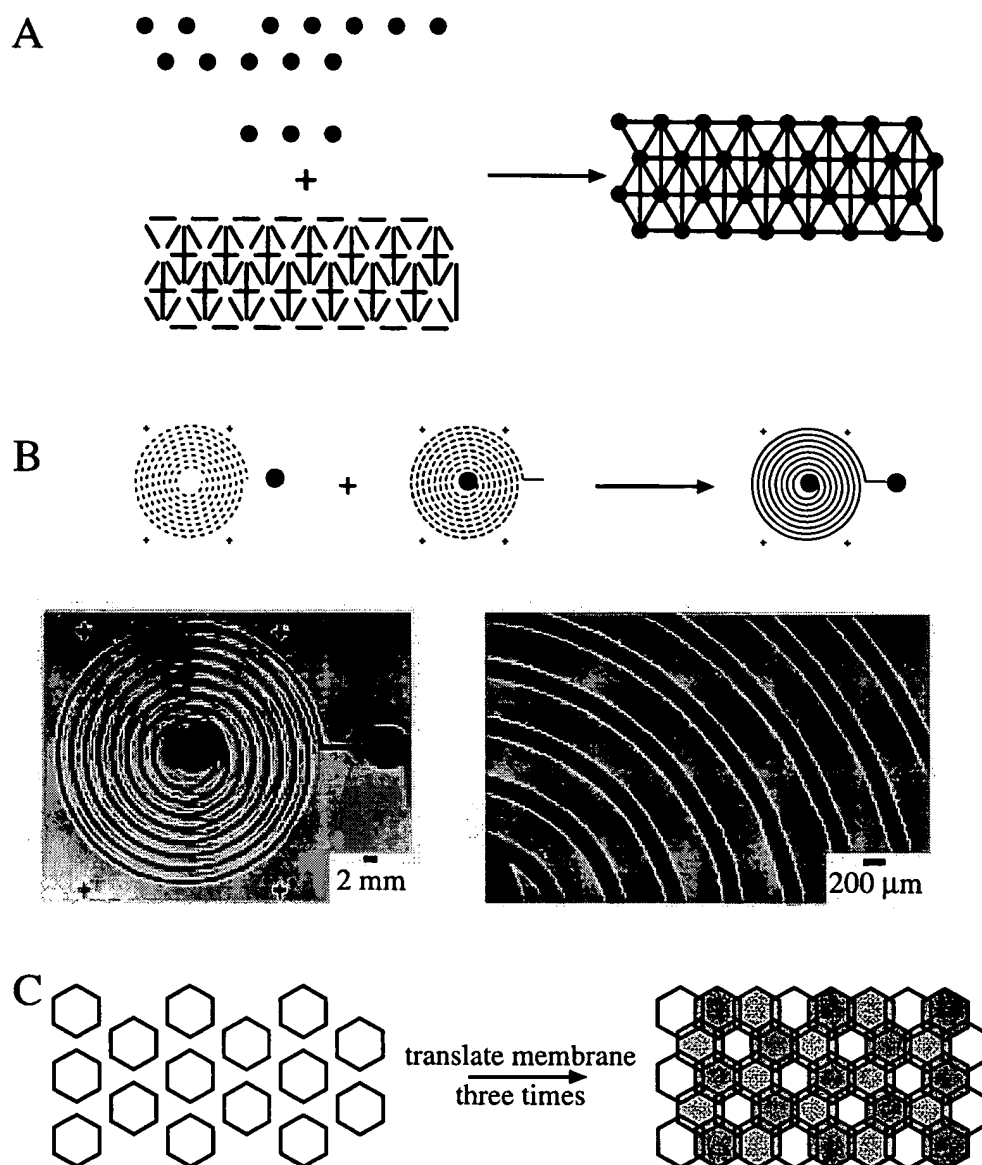


Figure 6. Two membranes can be used to produce arbitrarily complex structures. (A) Design for a pair of membranes based on a triangular lattice that can produce regular networks of wires. (B) Design for a pair of membranes that can produce a planar spiral and a photograph of a spiral produced by this method. (C) Three membranes can be used to pattern all space. Design for a set of membranes based on a grid of tessellated hexagons. Each membrane has only every third hexagon present.

membrane with this pattern were formed, it would be continuous but would tend to distort. We have demonstrated that the serpentine structure is electrically continuous and we can electroplate gold onto it to lower its resistance. After the structure was electroplated to $\sim 8 \mu\text{m}$ thick, the resistance between the points marked B and E was $\sim 1.7 \Omega$ (subtracting the contribution of the indium connectors)—given the geometry of the wires ($L \sim 20 \text{ mm}$; width $\sim 50 \mu\text{m}$) this value gives a resistivity ($3.4 \times 10^{-8} \Omega \text{ m}$) on the same order of magnitude as bulk gold ($2.3 \times 10^{-8} \Omega \text{ m}$).³² We have also patterned surfaces using two membranes at the same time to create patterns of red, blue, and green (RGB) electroluminescent materials;²⁴ one membrane was in direct contact with the substrate and defined the composite pattern; a second

membrane was sealed on top of the first and defined the region of the composite pattern over which each color was deposited.²⁴

As the examples in Figure 5 illustrate, when using multiple membranes, in addition to the considerations for each membrane itself, it is important that there is continuity between the layers deposited in separate steps, particularly if the final structure is to be conductive. To ensure this continuity, we designed each membrane of the set so that each element of an arbitrary grid was slightly oversized to guarantee overlap between features.

We have considered how two or more membranes can, in general, be used to make more complex structures in two dimensions. For example, to create simple electrical circuits or arrays of interconnected wires, a pair of membranes based on a triangular repeat pattern offers considerable flexibility (Figure 6A). The first membrane consists of an array of dots arranged on a triangular lattice. The second membrane contains lines/rectangular slots that join adjacent dots and also allow connections between dots separated by one row. With this pair of membranes,

(32) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990. Contributions to the differences in resistivity come from the gold/titanium/gold junctions that are present where the patterns join and that result in variations in thickness. These contributions are small when compared to the thickness of gold ($\sim 8 \mu\text{m}$) after electroplating.

we can produce the required network of intersecting wires by choosing which members of the complete set of connecting lines/dots are present in a given membrane. With this scheme, up to four lines can intersect at different angles (including right angles), and by varying the dimensions of the circles in the first membrane while holding the period constant, contact pads can be produced.

A pair of membranes based on the triangular lattice described above cannot, however, produce randomly oriented wires with curvature or wires that intersect more than four at a time. This type of structure can, in general, be produced using two membranes; there are two issues to consider: (i) how to produce lines, and (ii) how to deal with the intersection of lines. If we first consider the lines: any line can be broken down into two (overlapping) sets of self-supporting segments that two membranes can reconstruct. Figure 6B shows a planar spiral formed using this approach that was constructed from the two membranes shown. The pattern was designed so that there was overlap between adjacent slots to ensure electrical continuity. As the enlarged image shows, the line width of the wire is $\sim 200\ \mu\text{m}$ and the two membranes were registered to within $\sim 20\ \mu\text{m}$ over a square centimeter. We used a set of translation and rotation stages and a stereoscope to align the patterns by eye; using a more sophisticated apparatus, we anticipate that we could align smaller structures over larger areas. In a more complex design, considering the intersection of two wires, a cross at the intersection will suffice. If four lines come together, two crosses (one on each membrane) will work. For more lines intersecting, a multipointed star or circle at the center of the intersection would be appropriate.

In most cases, particularly when a pattern requires discrete wires, two appropriately chosen membranes will suffice. A pair of membranes cannot, however, pattern an entire plane because of structural constraints on each membrane, i.e., it must be continuous and self-supporting. If a membrane is to be continuous and self-supporting, then the features in the mask are (by necessity) discrete, e.g., an array of crosses. If this membrane were used with a second membrane to fill in the remainder of space, the second membrane would have to be the inverse of the first (with oversizing to ensure overlap) and so would have to consist of discrete elements, e.g., an array of crosses, and therefore could not be self-supporting.

In cases where all of a two-dimensional plane needs to be patterned or where continuous areas are required, three membranes are necessary. One design for such a set of membranes would be to use a grid of tessellated hexagons in which only every third hexagon was present and where the dimensions of the hexagons were slightly larger than the cell spacing to ensure overlap (Figure 6C)—other sets of membranes are also possible and might be selected depending on the needed pattern.

Using Multiple, Elastomeric Membranes To Pattern Both the Interior and Exterior of Curved Substrates. The flexibility of the elastomeric membranes makes them amenable to patterning curved substrates—for example, they will conform to and seal against the interior or exterior surfaces of a capillary. Using a single membrane with slots oriented at an appropriate angle that has been wrapped around a capillary, we deposited metal lines onto the exterior of a glass capillary. We then removed the membrane and then wrapped a similar membrane around the capillary so that the end of each slot was aligned with the patterned metal lines. Depositing metal and then performing dry lift-off produced a solenoid (Figure 7A). The spiral was electrically continuous and can be electroplated. Figure 7B shows the

concave surface of a section of a glass rod that we patterned with metal features by sealing a membrane against the substrate, depositing metal through it, and then performing dry lift-off.

Conclusions

We have demonstrated that it is possible to produce microstructures as small as $5\ \mu\text{m}$ in a variety of materials by using elastomeric membranes either as dry resists or for dry lift-off procedures. This procedure will, we believe, be particularly useful for patterning materials that are sensitive to the processing conditions used in conventional fabrication (e.g., organometallic molecules or biological materials) or that require processing steps that are not compatible with the materials, such as photoresist, used in fabrication (e.g., the high pH needed to process ORMOSIL ceramics). We anticipate that these membranes, with the right combination of materials, could be used to produce, for example, a transistor from only polymeric components with feature sizes less than $10\ \mu\text{m}$. We believe that these membranes will also be important for patterning on the interior and exterior of curved substrates: while soft lithography³³ has been used pattern metal or photoresist on the exterior of curved substrates, we are unaware of any technique, other than this one, that allows the formation of patterns in other materials on such substrates. We note that the use of these membranes for patterning is similar to screen printing, which is also used to pattern a range of materials.¹¹ The main advantage of using the membranes over screen printing is the small ($5\ \mu\text{m}$) features that can be created: the minimum mesh size of screens means that the smallest features that can be created practically by screen printing is $75\ \mu\text{m}$.

This technique is, however, not competitive with photolithography for patterning planar structures of materials usually used in microfabrication at the sub-micrometer scale. While we do not believe that $5\ \mu\text{m}$ represents an intrinsic lower limit, given that the optimal aspect ratio for masters (and membranes) is unity (or less), as features become smaller, the membranes become thinner and less easy to manipulate, making fabrication at the submicrometer scale difficult. Also, given the structural limitations on the elastomeric membranes, and the need to use two membranes to make large networks of wires, this method will not be the one of choice for producing metallic wires on planar substrates.

One issue in using elastomeric membranes is their deformability: in some cases (patterning nonplanar substrates), this property is an asset, in others (producing small features that are regularly spaced), it is a limitation. In the later cases, this problem can be addressed by using two-layer membranes that have both the rigidity of an epoxy layer and the sealing properties of a PDMS layer. We have demonstrated that when aligning membranes to within $20\ \mu\text{m}$ (over distances of $20\ \text{mm}$) under a stereoscope the distortion is not significant. To produce complex structures with feature sizes less than $\sim 10\ \mu\text{m}$, the problems of distortion and registration will need to be reexamined and an apparatus similar to a mask aligner or pattern recognition system will be required.

Experimental Section

Materials. We used the SU-8 series (5 and 50) photoresist as received from Microlithography Chemical Corp., Newton, MA. The photomasks for performing photolithography were either

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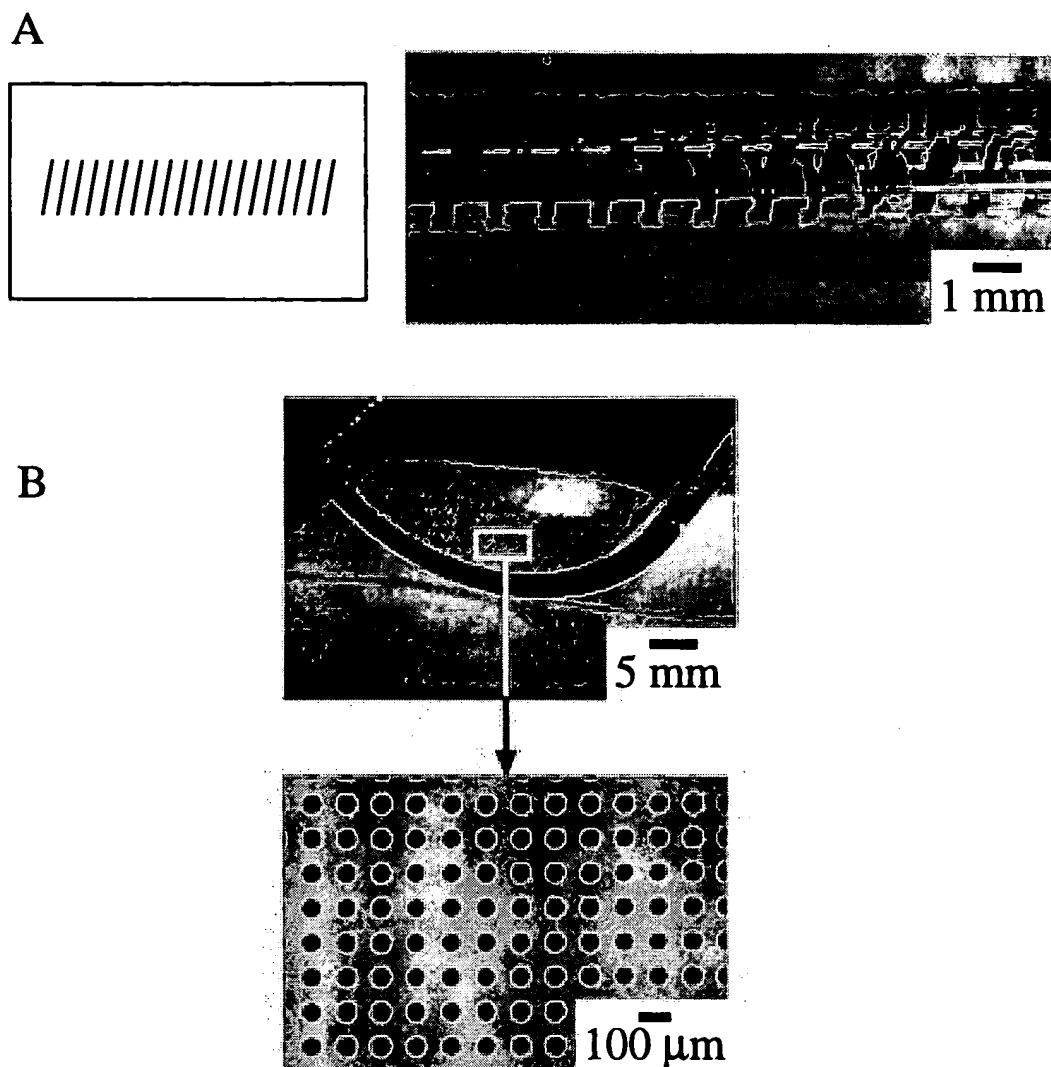


Figure 7. Using elastomeric membranes to pattern on the interior and exterior of cylindrical substrates. (A) Design for membrane used to produce a solenoid on a cylindrical substrate that has a series of parallel slots oriented at an appropriate angle. The optical micrograph shows a solenoid formed using this membrane. A set of metal lines was produced by wrapping the membrane around the exterior of the capillary, depositing titanium (5 nm) and then gold (200 nm) onto the capillary, and performing dry lift-off. The lines were joined to form a spiral by performing a second metal evaporation and dry lift-off step with a similar membrane that was aligned so that the ends of the slots in the membrane joined the existing metal lines. (B) Optical micrograph showing circles of gold (50- μm diameter) on the concave surface of a glass tube. We formed these structures by placing a membrane in contact with the tube, depositing titanium (5 nm) and then gold (20 nm) onto the substrate, and then performing dry lift-off.

rigid chrome masks (Advanced Reproductions, North Andover, MA; features $<50\ \mu\text{m}$) or transparencies (produced using Herkules PRO image setter, 3387 dpi, Linotype-Hell Co., Hauppauge, NY, by a desktop publishing company, Pageworks, Cambridge St., Cambridge, MA; features $>50\ \mu\text{m}$).

We used a poly(dimethylsiloxane) prepolymer (PDMS; Sylgard 184) as obtained from Dow Corning, Midland, MI, and an epoxy (Epo-tek UVO 114) from Epoxy Technology, Billerica, MA. All other chemicals were obtained from Aldrich Chemical Co.

Fabrication of Masters. The master consisted of an array of features in photoresist created on a silicon wafer. It was generated either by "rapid prototyping" (for feature sizes $>50\ \mu\text{m}$)²⁵—a method that uses a high-resolution transparency as the photomask for photolithography—or by performing standard photolithography with a chrome mask (for feature sizes $<50\ \mu\text{m}$). For feature sizes greater than $50\ \mu\text{m}$ (less than $50\ \mu\text{m}$), we used SU-8 50 (SU-8 5) resist. Spin-coating the resist at 5000 rpm for 40 s (2500 rpm for 40 s) produced a film approximately $50\ \mu\text{m}$ thick ($5\ \mu\text{m}$ thick). After baking the resist at $105\ ^\circ\text{C}$ for 15 min (5 min), we exposed it to UV light for 1 min (10 s) through a mask using a Karl Suss mask aligner. We developed the features in propylene glycol methyl ether acetate (PGMEA) for ~ 5 min (1 min) after the wafer had been baked for 15 min (5 min) at $105\ ^\circ\text{C}$.

Surface treatment of the silicon wafer by exposure to the vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technology, Bristol, PA) in a vacuum desiccator prevented adhesion of the elastomer to the wafer during the next step.

Fabrication of Elastomeric Membranes (Figure 1). Spin-coating a liquid prepolymer of PDMS onto a master created an elastomeric membrane. The rate of spinning was set so that the thickness of the layer of PDMS was less than the height of the posts of photoresist: for example, for posts $50\ \mu\text{m}$ high, we spin-coated PDMS at 3000 rpm for 60 s to produce an approximately $45\ \mu\text{m}$ thick film; for posts $5\ \mu\text{m}$ high, we spin-coated a 1:4 mixture of PDMS/toluene for 60 s to yield a film less than $5\ \mu\text{m}$ thick. The PDMS was cured for 1 h at $65\ ^\circ\text{C}$. In the case of the thinner films ($<50\ \mu\text{m}$), we typically "painted" a thicker (1 mm) layer of the liquid prepolymer around the outside of the pattern to form a supporting frame around the pattern. This thicker layer helped to release the polymer from the master and minimized the distortion of the membrane when it was removed from the master. In some cases, to remove low molecular weight polymer from the membrane, we soaked it in chloroform for 3 h and then dried it overnight at $100\ ^\circ\text{C}$. We have produced membranes containing arrays of holes with diameters varying from $3\ \mu\text{m}$ to $1\ \text{mm}$.

To make two-layer membranes (with PDMS and epoxy layers), we did not form a supporting border of PDMS around the features;

instead, after curing the PDMS, we oxidized its surface for 30 s using a plasma cleaner (Harrick, PDC-23G) and then spin-coated (800 rpm for 35 s) onto the wafer a layer of epoxy ($\sim 10\ \mu\text{m}$ thick; Epotek UVO114, Epoxy Technology, Billerica, MA). Exposure to UV light for ~ 10 min cured the layer of epoxy. We produced rigid borders around these membranes by dispensing epoxy from a syringe to form a supporting frame around the features. Further exposure to UV light for ~ 10 min hardened the second layer of epoxy.

Handling of Elastomeric Membranes. To release the membranes, we cut around the border with a scalpel and then, using a pair of tweezers, peeled the membrane slowly from the master. We brought the membranes into contact with the substrate to be patterned using a pair of tweezers. On contact with the substrate, the membrane wet the surface and formed a reversible seal with it. If the membrane was not lying flat on the substrate to begin, then we removed the membrane with tweezers, replaced it on the surface, and allowed it to reseal. In cases when using solvents was not problematic, we often placed a drop of 2-propanol on a membrane in contact with a substrate; this procedure made it easier to ensure that the membrane was lying flat on the substrate.¹⁴ In the cases where registration of the membrane to an existing pattern was required, we performed the sealing steps under a stereoscope (Wild MZ6 stereoscope, Leica, Heidelberg, Germany) using a set of translation and rotation stages (Newport Corp., Irvine, CA).

Using Elastomeric Membranes as Dry Resists. (a) For Dry Etching. We placed a PDMS membrane containing circular holes ($3\ \mu\text{m}$ diameter, separated by $3\ \mu\text{m}$) in conformal contact with a silicon substrate. Exposure of the masked substrate to a reactive ion etching plasma (SF_6 (30 sccm) and O_2 (3 sccm)) for 8 min resulted in the formation of microwells $\sim 1\ \mu\text{m}$ deep. Removal of the mask revealed that the etched wells were in register with the channels in the PDMS mask.

(b) For Electrodeposition. A PDMS membrane containing circular holes ($50\ \mu\text{m}$ diameter, separated by $50\ \mu\text{m}$) sealed against a gold-coated silicon wafer when brought into contact with it. This procedure formed "wells" whose sides were defined by the channels in the membrane and whose bottoms were defined by the gold surface. We oxidized the surface of the PDMS membrane for 30 s using a plasma cleaner (Harrick, PDC-23G) to render the surface of the membrane hydrophilic so that the plating solution would wet it. A drop of triethylene glycol was then placed on top of the membrane, and air trapped in the wells was removed under vacuum (10–20 s); this step ensured that each well contained solution, not a trapped air bubble. Electroplating silver from a plating bath (Technic Silver E2, Technic, Providence, RI; current density $\sim 20\ \text{mA}/\text{cm}^2$) onto the regions of the gold surface in register with the channels in the PDMS produced metallic microstructures on the conductive substrate. After removal of the mask, these structures remained on the surface.

(c) By Sol–Gel Methods. Oxalic acid (0.7 g, 0.1 M, 0.07 mol) and 3-glycidopropyltrimethoxysilane (5 g, 0.02 mol) were mixed for 1 min and allowed to stand for at least 6 h.¹⁸ We sealed a PDMS membrane containing circular holes ($50\ \mu\text{m}$ diameter, separated by $50\ \mu\text{m}$) against a silicon substrate and oxidized the sample for ~ 1 min to render the membrane hydrophilic and easily wet by the solution. We placed one drop ($\sim 50\ \mu\text{L}$) of ammonium hydroxide into the solution ($\sim 1\ \text{mL}$) and, after mixing, placed a drop ($\sim 0.5\ \text{mL}$) of it on top of the masked substrate so that the membrane was completely covered. After approximately 5 min, the silicon substrate and mask were tilted to drain the liquid from the surface and then left overnight at room temperature. Under basic (pH ~ 11) conditions, the acidic solution gelled by hydrolysis and polycondensation to yield a glassy material: removal of the PDMS membrane from the silicon substrate revealed glassy structures in register with the channels in the membrane. We dried the structures at $60\ ^\circ\text{C}$ for 72 h.

(d) Hydrogels by Dewetting. We sealed a membrane ($50\ \mu\text{m}$ circles, spaced by $50\ \mu\text{m}$) on a glass slide that had been cleaned in piranha solution (concentrated $\text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2$ (3:1); *Cautions: piranha solution can react violently with organic materials and should be handled with care*) and then oxidized for 60 s in a plasma cleaner: this step rendered the membrane and substrate hydrophilic and easily wetted by the solution. We then placed a drop of a solution of gelatin (KNOX, Nabisco Inc., East Hanover,

NJ) at $60\ ^\circ\text{C}$ on the sample so that the membrane was completely covered with solution. After the sample was degassed under vacuum (10–20 s) to remove air trapped in the wells formed by the membrane in contact with the substrate, we placed the sample back in the oven at $60\ ^\circ\text{C}$ and allowed the solution to dewet from the substrate, leaving solution in the wells. We then left the sample at room temperature to allow the solution to set and then removed the membrane, leaving an array of patterned gelatin on the substrate.

Using Elastomeric Membranes for Dry Lift-Off. (a) Metals by Electron-Beam Evaporation. We sealed an elastomeric membrane containing $50\ \mu\text{m}$ circular holes (spaced by $50\ \mu\text{m}$) against a silicon wafer. Deposition of a thin layer of titanium (5 nm, $\sim 0.1\ \text{nm/s}$) followed by a layer of gold (50 nm, $\sim 0.3\ \text{nm/s}$) by electron-beam evaporation (base pressure $\sim 5 \times 10^{-7}$ Torr) onto the masked substrate resulted in metal on both the substrate and the membrane. Peeling away the elastomeric membrane from the substrate using a pair of tweezers left gold on the substrate in the regions that were in register with the circular holes in the membrane.

(b) By Thermal Evaporation of Electroluminescent Organometallic Molecules. A PDMS membrane, containing either an array of circular holes ($3\ \mu\text{m}$, spaced by $3\ \mu\text{m}$) or an alphanumeric pattern (smallest dimension $\sim 100\ \mu\text{m}$) sealed conformally against a silicon substrate when brought into contact with it. An electroluminescent material, tris(8-hydroxyquinoline)-aluminum (Alq_3 , 50 nm) was deposited by thermal evaporation (rate of deposition $\sim 0.5\ \text{nm/s}$; base pressure $\sim 5 \times 10^{-6}$ Torr) onto the membrane and substrate. Peeling the elastomeric membrane from the substrate left features of Alq_3 on the surface patterned as circles or alphanumeric characters.

(c) Biological Materials by Nonspecific Adsorption. We sealed a PDMS membrane containing circular holes ($3\ \mu\text{m}$ diameter, separated by $7\ \mu\text{m}$) against a gold-coated surface coated with a monolayer of hexadecanethiol. A buffer solution (100 mM Tris, 20 mM boric acid) containing 2 mg/mL of a protein, bovine carbonic anhydrase, fluorescently labeled with fluorescein isothiocyanate was prepared. We placed a drop ($\sim 1\ \text{mL}$) of the solution of protein on the substrate to fill the wells defined by the holes in the membrane and the hydrophobic gold surface; trapped air was removed by vacuum. Protein deposited on all regions of the membrane and exposed substrate; the conformal seal ensured that liquid did not wick onto the region of the substrate covered by the membrane. After 2 h, the substrate and mask were washed with buffer solution and dried in a stream of N_2 . After dry lift-off, fluorescence microscopy revealed that protein had adsorbed only to the hydrophobic gold surfaces in register with the channels in the membrane.

(d) Conducting Polymer Precursor by Chemical Vapor Deposition. We brought a membrane ($50\ \mu\text{m}$ holes, spaced by $50\ \mu\text{m}$) into contact with a substrate (Si or indium tin oxide) and placed it into the CVD system (base pressure ~ 0.03 Torr). Details of the system are described elsewhere.^{34,35} We prepared PPV from a dichloro-*p*-xylene starting monomer, in a method similar to CVD of parylene.³⁴ The monomer (α,α' -dichloro-*p*-xylene) was heated to $60\ ^\circ\text{C}$ and brought to a furnace where it was pyrolyzed at $675\ ^\circ\text{C}$ to form a chloro-*p*-xylene. This material was transported at low pressures (~ 0.1 Torr) to the deposition zone by an Ar carrier gas (flow rate $\sim 8\ \text{sccm}$) where it condensed on the substrate ($25\ ^\circ\text{C}$) and polymerized to form a PPV precursor (a chlorinated poly(1,4-xylene)). After heating the substrate at $150\ ^\circ\text{C}$ for ~ 1 h to partially convert the precursor, we performed dry lift-off. Further heating to $250\ ^\circ\text{C}$ fully converted the precursor to PPV.

Formation of Complex Structures by Dry Lift-Off. We performed a first dry lift-off step after evaporating an adhesion promoter (Ti, 5 nm; rate $\sim 0.1\ \text{nm/s}$), followed by gold (50–200 nm; rate $\sim 0.3\ \text{nm/s}$) through the first membrane. We then aligned a second membrane to the first under the stereoscope, sealed the membrane against the substrate, and repeated the evaporation and dry lift-off procedure. In the case of the nonplanar substrates,

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we wrapped the membrane around the exterior of the capillary under the stereoscope. Using a rotation stage to ensure deposition around the entire capillary, we evaporated titanium (5 nm; 0.1 nm/s) and gold (50–200 nm; 0.3 nm/s).³⁶ We then removed the membrane and realigned a second membrane to it under the stereoscope and then carried out a second evaporation.

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